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Composition dependence of the heat capacity jump in Ge-Se-In chalcogenide glasses

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Chalcogenide glasses are obtained by mixing the chalcogen elements, viz., S, Se, and Te, with elements of the periodic table such as Ga, In, Si, Ge, Sn, As, Sb, and Bi, etc. In these glasses, short-range inter-atomic forces are predominantly covalent: strong in magnitude and highly directional, whereas weak van der Waals' forces contribute significantly to the medium-range order. These materials exhibit unique physical properties that make them good candidates for several potential applications such as infrared transmission and detection, threshold and memory switching, etc. [1]. In this respect, the analysis of the compositional dependence of their properties is an important aspect of their study.

Recently, we have reported the compositional dependence of the peak crystallization temperatures [2], the free volume percentage [3], the atomic density [4], the compactness [5], the glass transition temperatures [6], and the plasmon energies [7] for Ge-Se-In system.

Differential scanning calorimetry (DSC) is an extensively used technique for the investigation and interpretation of thermal events in materials. In the present work, we have used DSC to establish the heat capacity jump, ΔC_p at $T_g[\Delta C_p = C_{pl} - C_{pg}$, C_{pl} and C_{pg} refer to C_p values of the supercooled liquid and the glassy state, respectively], as a function of composition for Ge-Se-In glasses.

Melt-quench technique was used to prepare glasses of $Ge_xSe_{94-x}In_6$ $(4 \leq x \leq 34)$ and $Ge_ySe_{88-y}In_{12}$ $(7 \leq y \leq 26)$. High-purity (5N pure) elemental materials were weighed according to their atomic percentages and loaded in cylindrical silica glass tubes (inner diameter = 8 mm). The tubes were then sealed under a vacuum of 10^{-5} torr and transferred to a furnace. The temperature of the furnace was raised to 450 °C and the tubes were kept at this temperature for 24 hr. Afterwards, the temperature of the furnace was raised to 850 °C for 48 hr and the tubes were frequently shaken to homogenize the melt. The quenching was done in cooled water.

For DSC measurements, a Perkin-Elmer series 4 calorimeter was used. Experiments were run under a nitrogen flow at a heating rate of 20 K min^{-1}. A small lump of glass (20–30 mg) was sealed in an aluminum pan and run against an empty aluminum pan. Calibration of the calorimeter was performed with regard to temperature and enthalpy of indium as standard material.

A typical DSC scan for $Ge_{34}Se_{60}In_6$ glass is shown in Fig. 1. The ΔC_p at T_g is evaluated using the relation [8]

$$\Delta C_p = \left(\frac{\Delta H}{m}\right)\left(\frac{1}{\alpha}\right) \quad (1)$$

where ΔH is the change of heat flow through a sample of mass m and α is the heating rate. The value of the normalized change of heat flow $(\Delta H/m)$ is obtained as indicated on Fig. 1.

The mean coordination number, Z, was evaluated according to the normal procedure [9]. For $Ge_xSe_yIn_{1-x-y}$ glasses, Z is given by

$$Z = x\mathrm{CN}\,(\mathrm{Ge}) + y\mathrm{CN}\,(\mathrm{Se}) + (1-x-y)\,\mathrm{CN}\,(\mathrm{In}) \quad (2)$$

It is generally accepted that coordinations of Ge and Se conform with Mott's "8-N" rule [10], where N is the number of outer shell electrons in a given atom. Therefore, coordinations of 4 for Ge and 2 for Se were used in the evaluation of Z. A coordination number of 3 for In, a value that was obtained by us [11] from extended X-ray absorption fine structure (EXAFS) measurements from the In K-edge, was also used for the evaluation of Z.

The chief result of this work is depicted in Fig. 2. It is seen that ΔC_p possesses a local minimum in the vicinity of $Z \cong 2.4$. This result is rationalized as follows.

On the basis of extensive investigations, Angell [12] classified the glass-forming liquids according to the temperature dependence of their viscosity. Liquids exhibiting an Arrhenius temperature dependence of the viscosity are defined as strong glass-forming liquids. Those liquids which exhibit a non-Arrhenius dependence (for instance, described by a Vogel–Tammann–Fulcher equation) are declared fragile glass-forming liquids. It is well recognized that oxide glass formers such as GeO_2 and SiO_2 with well-formed tetrahedral network structures and directional bonds belong to the category of strong-forming liquids. On the other hand,

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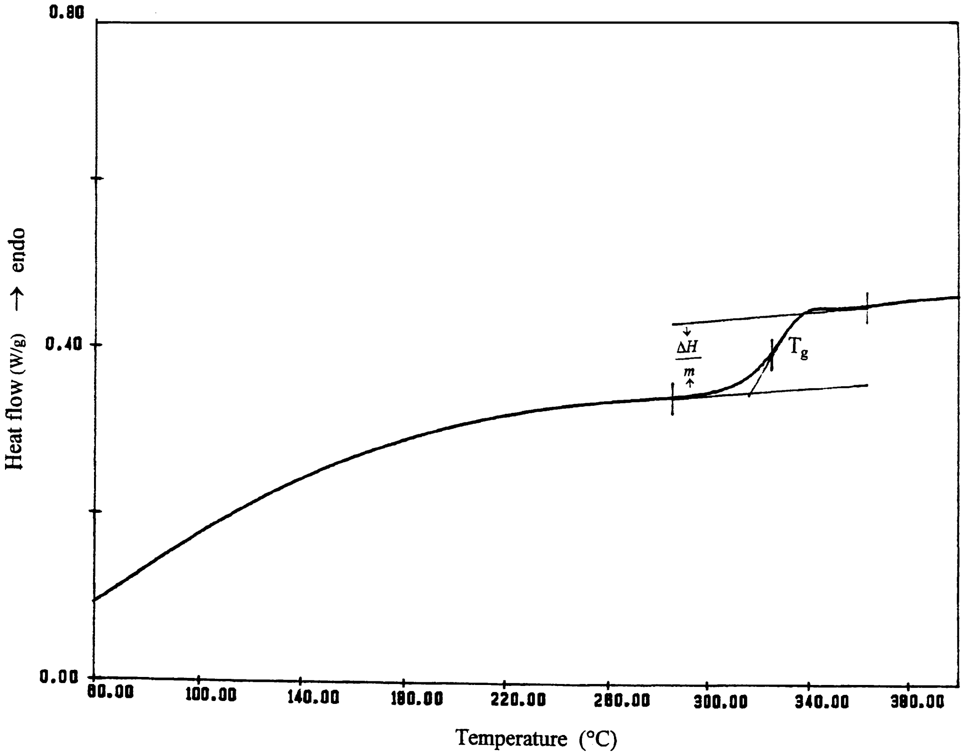

Figure 1 A DSC scan obtained from $Ge_{34}Se_{60}In_6$ glassy composition.

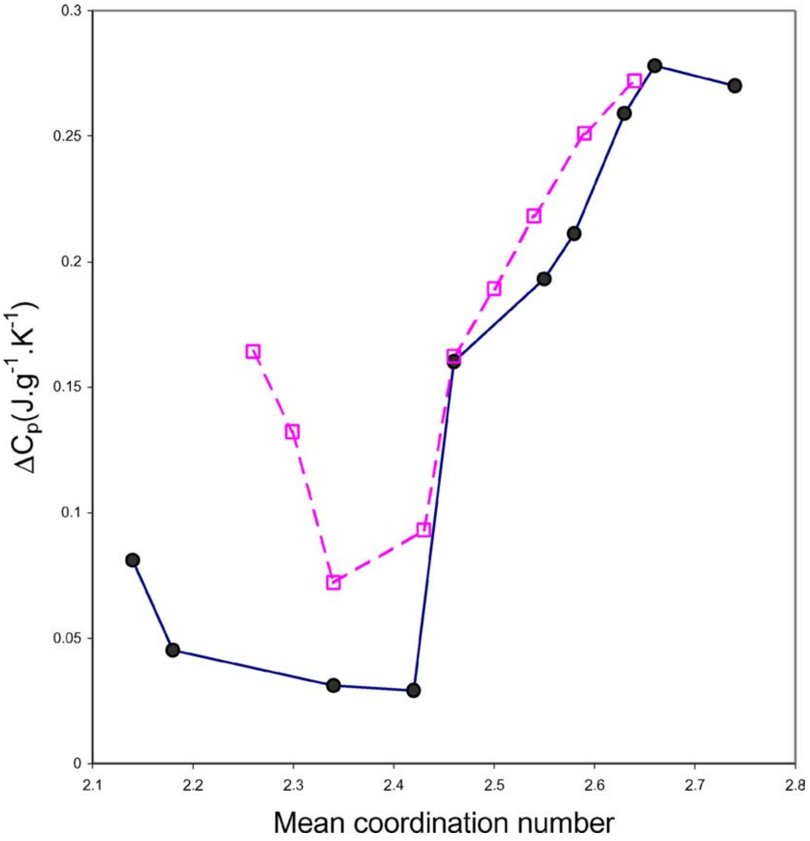

Figure 2 ΔC_p versus Z for Ge-Se-In glasses. The ΔC_p values for $Ge_xSe_{94-x}In_6$ and $Ge_ySe_{88-y}In_{12}$ are represented by circles and squares, respectively.

ionic glass formers with poor directionality in bonding are fragile-forming liquids. Recently, the strength–fragility concept of glass-forming liquids has been extended to the glassy state [13]. The values of ΔC_p at T_g can also be connected to this strength-fragility concept. As pointed out by Angell [12], glasses exhibiting a high ΔC_p value ($\Delta C_p \geq 0.3$ J K^{-1} g^{-1}) are far from their thermodynamic equilibrium (this equilibrium is obtained by extrapolation of the liquid-like state in the temperature domain of the glassy state). These glass-forming liquids and the associated glasses are defined as thermodynamically fragile. At the opposite, a low value of ΔC_p at T_g must lead to strong thermodynamic behaviors.

The following correlation [14] of a minimum fragility with a minimum of ΔC_p at T_g is to be expected from the Adam–Gibbs equation [15]

$$\eta = \eta_0 \exp\left[\frac{A}{T\ S_c}\right] \tag{3}$$

where $A \cong \Delta\mu \ln 2$ ($\Delta\mu$ is the potential barrier hindering rearrangements) and S_c is the configurational entropy given by

$$S_c = \int_{T_K}^{T} \left(\frac{\Delta C_p}{T}\right) dT \tag{4}$$

where T_k is the Kauzmann temperature. Thus, when ΔC_p is very small, S_c is almost temperature independent and Equation 3 follows an Arrhenius form. On the other hand, when ΔC_p is bigger [16], with a functional form of the type B/T [17], the Vogel–Tamman–Fulcher law, characteristic of fragile glass-forming liquids, is recovered from Equation 3.

The high value of ΔC_p for fragile glasses is due to the addition of translational and/or rotational modes made available by the breakage of bonds forming the glass network. An immediate consequence of the high values of ΔC_p at T_g for fragile glasses is that their structure breaks down rapidly with increasing temperature near and above T_g and thus a large number of configurations are made available for the glass (i.e., there is a marked structural rearrangement as the equilibrium liquid transforms to nonequilibrium glass). On the contrary, the low ΔC_p at T_g for strong glasses indicates that their structure resists changes with increasing temperature and undergoes fewer configurational changes near and above T_g (i.e., there is not much difference between the structures of the melt and the glass).

As it is evident from Fig. 2, all the studied Ge-Se-In glasses can be declared thermodynamically strong. Furthermore, the minimum of ΔC_p at T_g in the vicinity of $Z \cong 2.4$ (see Fig. 2) indicates that the glass composition with this Z value possesses the minimum fragility. Thus, the strongest thermodynamic character is reached at about $Z \cong 2.4$. This result is in harmony with that of Philips [18] that the best glass former (perfect glass) is found at the composition with $Z = 2.4$, where the number of Lagrangian constraints per atom are matched with the three available degrees of freedom. Therefore, it is concluded that at $Z \cong 2.4$ the glass-forming liquid has a minimized crystallization tendency by virtue of having reduced accessible structural or configurational reorderings in the supercooled liquid region.

Similar minima of ΔC_p at T_g at $Z = 2.4$ have been reported in Ge-As-Se [14], Ge-Se and Ge-Se-Sb [19], and Ge-Se and Ge-As-Se [20] and attributed to the minimum fragility for the glass composition with this mean coordination number.

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